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Photoconductive Properties and C₆₀ Doping Effect of Polyacetylene Derivatives

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Polyacetylene, (CH)_x, is the simplest conjugated polymer and is chain-like conducting polymer from which the conjugated system generally developed in the shape of one-dimensional chain. By π electrons which are contributed to the double bonds of the conjugated system, polyacetylene has the unique characters which are not seen to the usual insulating polymer which has only σ electrons. A photoconductive phenomenon is the one character. It is the phenomenon in which an electron-hole pair generates and it flows in an external circuit as a career, by exciting with the light of the energy more than forbidden bandgap to a conducting polymer.

On the other hand, fullerene (C₆₀) has good symmetry and unique properties for light. Additionally, when C₆₀ is used for conducting polymers, C₆₀ plays a role of a weak dopant: some small charge transfer is possible in conducting polymers with high enough top of valence band even under dark conditions, while in conducting polymers with much lower valence band, only photo-induced charge transfer occurs between C₆₀ and conducting polymers, resulting in the quenching of photoluminescence and also enhancement of photoconductivity.

In this study, we discussed the photoelectronic properties, mainly photoconductive properties, of monosubstituted polyacetylenes and disubstituted polyacetylenes, and C₆₀ doping effect of these polyacetylenes.

The poly(phenylacetylene) (PPA) derivatives such as poly(m-trimethylsilyl phenylacetylene) (PPA-mSiMe₃), poly(o-trimethylsilylphenylacetylene) (PPA-oSiMe₃), poly(o-(dimethylphenylsilyl)phenylacetylene) (PPA-oSiPMe₂), and the poly(diphenyl acetylene) (PDPA) derivatives such as poly(1-phenyl-2-p-t-butylphenylacetylene) (PDPA-tBu), poly(1-phenyl-2-p-n-butylphenylacetylene) (PDPA-nBu), poly(1-phenyl-2-p-n-hexylphenylacetylene) (PDPA-nHx), poly(1-phenyl-2-p-n-octylphenylacetylene)

(PDPA-nOc), were studied, the molecular structures of which are shown in Figure. 1.

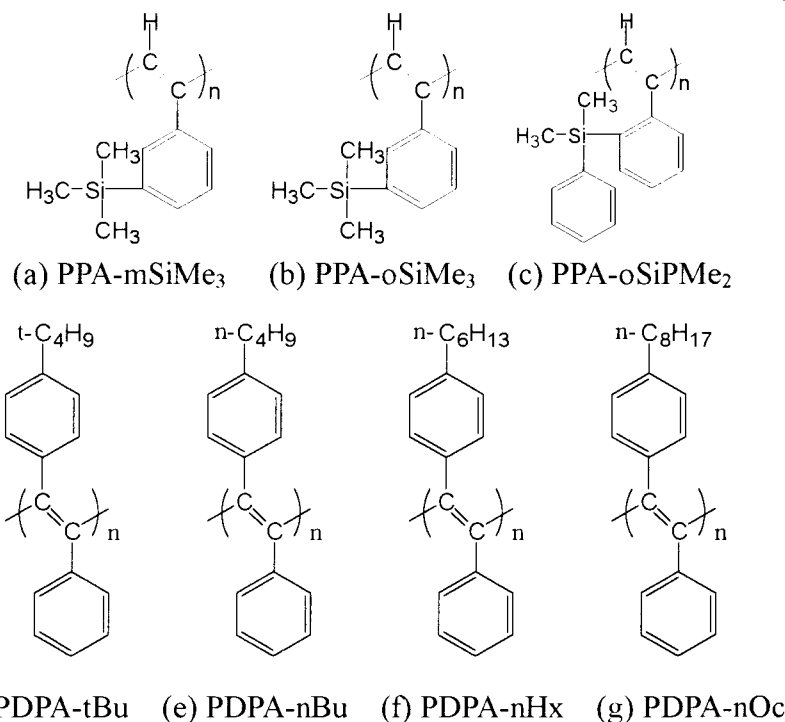


Fig.1 Molecular structures of PPA derivatives and PDPA derivatives used in this study.

Thin films of the polymers were prepared by casting of polymer solution on appropriate substrates such as quartz plates. Absorption (ABS) and Photoluminescence (PL) spectra of these thin films were measured in vacuum at room temperature using spectrophotometers (Hewlett Packard HP 8452) and a fluorescence spectrometer (Hitachi F-4500), respectively.

Both C₆₀ and PPA or PDPA derivatives at appropriate molar ratios were dissolved in toluene, and the thin films were prepared by casting the solution onto an ITO coated quartz plates. Al deposited by vacuum evaporation on the polymer film as a second electrode. Photocurrent was measured by irradiation of an Xe arc lamp light onto the sample passing through a monochromator. Layer structure of sample was ITO / PPA or PDPA and C₆₀ / Al.

ABS spectra of PPA derivatives are shown at Fig.2(a), and ABS and PL spectra of PDPA derivatives are shown at Fig.2(b) and (c), respectively. Generally, trans-poly(acetylene) (t-PA) and PPA derivatives are considered to be nonluminescent conjugated polymers, because the lowest 2^1A_g exists below the lowest 1^1B_u exciton, $E(2^1A_g) < E(1^1B_u)$, and these conditions are the dipole forbidden characters of the lowest singlet state. On the other hand, PDPA derivatives shows strong PL intensity, because the electronic states changes from $E(2^1A_g) < E(1^1B_u)$ to $E(2^1A_g) > E(1^1B_u)$ by

two substitutions and these conditions are allowed character. Additionally, PDPA derivatives have alkyl chains at the para position of phenyl ring. From Fig.2(c), these alkyl chains being extended, PL intensity became stronger.

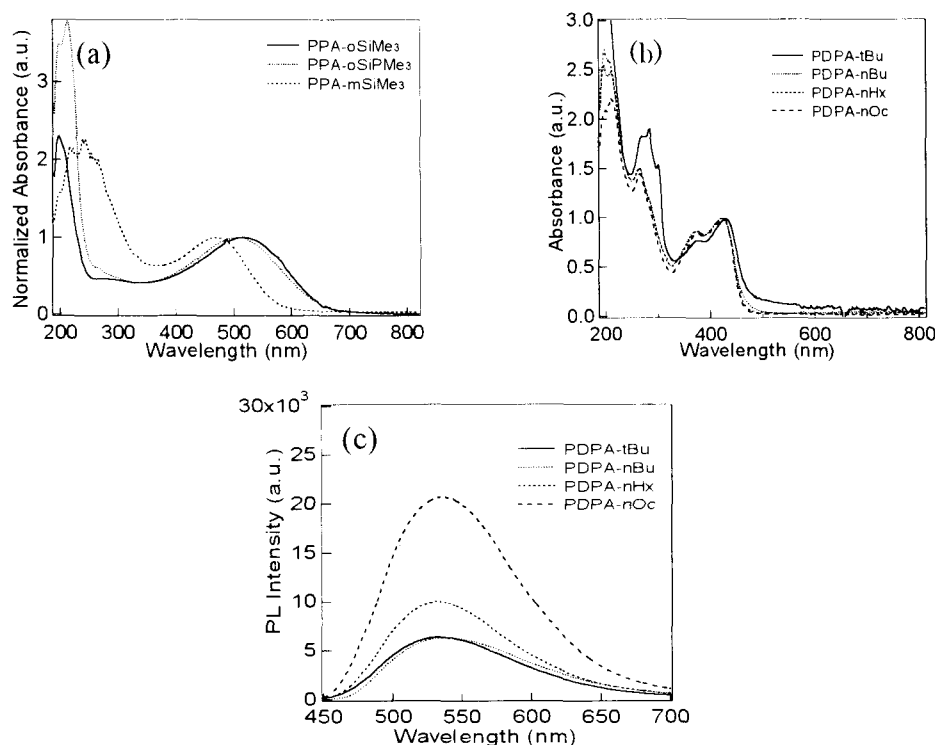


Fig.2 (a) Absorption spectra of PPA derivatives, (b) absorption spectra of PDPA derivatives, and (c) PL spectra of PDPA derivatives.

Figure3 shows the photocurrent and ABS spectra of PPA-oSiMe₃ doped with C₆₀. Generally, the photocurrent in conducting polymers appears, when the light of energy more than forbidden bandgap is irradiated, and the photocurrent increases near the energy region of forbidden bandgap. However, in the case of PPA-oSiMe₃ and PPA-oSiPMe₂ used in this study, photocurrent increased with the higher energy region than the forbidden bandgap. This results implies electronic state which contributes to photocurrent exists at higher energy than the forbidden bandgap.

On the other hand, photocurrent is remarkably enhanced upon C₆₀ doping, because of photo-induced charge transfer between C₆₀ and PPA-oSiMe₃. In these spectra we confirmed two peaks at around 320nm and 650nm.

Figure4 shows the PL and photocurrent spectra of PDPA-nBu with C₆₀ doping. The quenching of PL intensity and the enhancement of photocurrent were observed upon C₆₀ doping that seems to be the similar effects with the composite systems of general conducting polymer and C₆₀. Comparing with non-doped PDPA-nBu, the PDPA-nBu

with C_{60} concentration of 1mol% can be observed 100 times as much photocurrent.

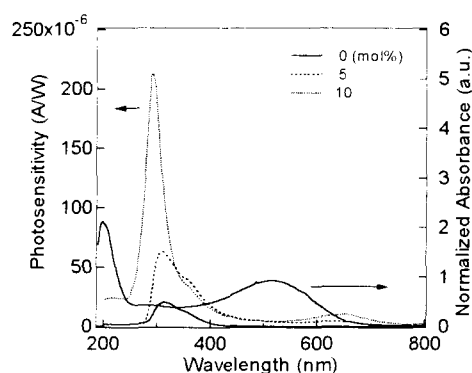


Fig.3 Photocurrent and absorption spectra of PPA-oSiMe₃ doped with C₆₀

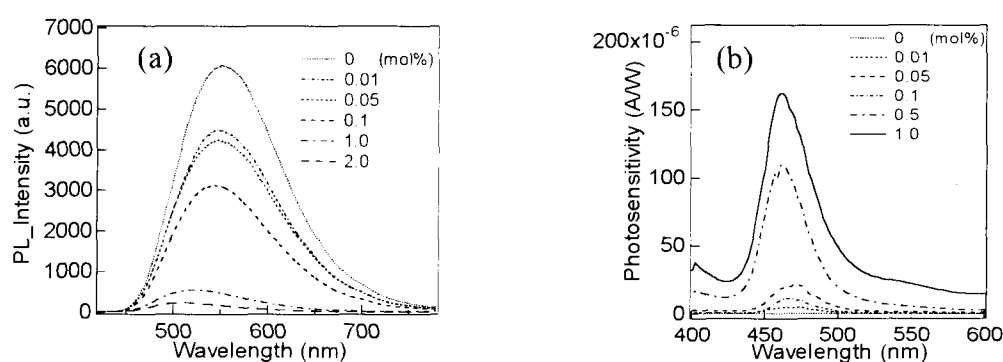


Fig.4 (a) PL spectra of PDPA-nBu with C₆₀ doping and (b) photocurrent spectra of PDPA-nBu with C₆₀ doping

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